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Copper–gallia interaction in $Cu–Ga_2O_3–ZrO_2$ catalysts for methanol production from carbon oxide(s) hydrogenation

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ABSTRACT

The impact of the interaction between copper and gallia was studied over a selected set of supported (2 wt%) Cu on Ga_2O_3, ZrO_2 and $Ga_2O_3–ZrO_2$ catalysts, which were employed in the methanol synthesis from CO_2 and CO mixtures. The higher initial rate of methanol production on the Cu/ZrO_2 catalyst was accompanied by an activity loss of ~35% after 5 h on stream. However, all the gallated catalysts were notoriously more stable (and selective) than copper on pure zirconia was. Temperature-programmed reduction in H_2, X-ray photoelectron spectroscopy and infrared spectroscopy of adsorbed CO results proved that temperatures higher than 553 K are needed to completely reduced Cu^{2+} to metallic Cu particles in the gallia-containing catalysts, which was attributed to the formation of a $CuGa_2O_4$ nanospinel. The ternary $Cu–Ga_2O_3–ZrO_2$ catalysts showed an intermediate behavior, quite dependent on the preparation protocol, which emphasizes the need for *tuning* the degree of Cu–oxides interactions. It is suggested that just a moderate copper–gallia interaction is beneficial in terms of both activity and selectivity but, also, that a detrimental loss of 'active' copper should be avoided.

1. Introduction

The synthesis of methanol by selective catalytic hydrogenation of carbon oxides using different catalysts has gained an increasing importance in the last decades. Methanol is still a large scale product of the chemical industry and is largely produced from 'synthesis gas' [$(CO + H_2)$ + some CO_2] [1]. Carbon dioxide is recognized as the most important greenhouse gas and any method for its chemical utilization and recycling by catalytic hydrogenation is of interest for contributing to mitigate the impact of excess CO_2 in the environment.

Point carbon dioxide emission sources are widespread. So, aimed to developing an efficient and selective catalytic system able to convert *both* CO_2 and CO to methanol under process conditions compatible with current industrial practice, unconventional $Cu–Ga_2O_3–ZrO_2$ catalytic materials were prepared by us [2]. Our motivation was that, in either case, the metal may supply the active sites to dissociate hydrogen [3], while Ga_2O_3 (which has an amphoteric character) favors the hydrogenation of CO_2 [4], and ZrO_2 (which also has an amphoteric character) affords the hydrogenation of CO to methanol [5].

In a previous paper, where the catalytic performance of these catalysts was evaluated using $CO_2/H_2/CO$ and $CO_2/H_2/He$ mixtures, it was found that the inclusion of gallium oxide (acting both as catalyst support and 'promoter' in the ternary $Cu–Ga_2O_3–ZrO_2$ materials) gave them a remarkable stability in the methanol synthesis [2]. Moreover, it was noticed that increasing Ga/Cu ratios lead to more selective catalysts as well. Most encouraging, also, was that the catalysts' activity of some of these materials was fairly close to those of commercial preparations.

The motivation of the present work was to gain more insight in regard to the substantial differences in the catalytic performance of these materials, on which the effects of support type (ZrO_2 or Ga_2O_3), the order of addition of copper and gallia, and the method of addition of the metallic function (that is, incipient wetness impregnation vs. ion exchange) were studied [2].

The most representative catalysts of the prepared set are hereby characterized, focusing mostly in the metallic function, seeking to evaluate the nature of the surface species and their evolution during oxidizing and/or reducing treatments with hydrogen and CO. This characterization aims to obtaining a detailed and systematic knowledge of the effects of the interactions between copper and the supports (ZrO_2, Ga_2O_3 and $Ga_2O_3–ZrO_2$) on the

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physicochemical characteristics of the catalysts, to get further understanding of the reactivity of $CO_2/CO/H_2$ mixtures on these promising catalysts.

2. Experimental

The set of Ga_2O_3/ZrO_2 supported copper catalysts was prepared using high purity $Cu(NO_3)_3{\cdot}2H_2O$ (99.00 wt% of copper). The pure supports, both of them obtained by sol–gel techniques in basic media, were also synthesized. Ammonium hydroxide and inert vessels were used, to avoid any undesired cationic promotion. Zirconia (S_{BET} = 25 m^2/g) was obtained by hydrolysis of Zr(IV) *n*-propoxide in 1-propanol (70 wt%), and gallia (S_{BET} = 90 m^2/g) was prepared by hydrolyzing $Ga(NO_3)_3{\cdot}9H_2O$ (99.999 wt% purity) with NH_4OH(aq.) in ethanol.

Gallia was supported on ZrO_2 by incipient wetness (IW) impregnation of gallium nitrate, followed by drying (383 K, 4 h) and calcining (673 K, 4 h), using several loadings (1, 6 and 9 wt%). These supports were labeled as *x*-Ga_2O_3/ZrO_2, where *x* stands for gallia weight percent. No significant decrease of the specific surface area of these materials with respect to the pure zirconia was observed.

Several series of catalysts were made, to evaluate the impact of the preparation methods on the interaction between copper and the different 'supportsí (ZrO_2, Ga_2O_3, *x*-Ga_2O_3/ZrO_2). In every case, 2 wt% Cu loading was used. In the first two series the metal was deposited either by incipient wetness impregnation (IW) of copper nitrate [IW Cu/Ga_2O_3, IW Cu/ZrO_2 and IW Cu/*x*-Ga_2O_3/ZrO_2] or by ion exchange (IE) of the copper salt, at pH 11, using NH_4OH(aq.) [IE Cu/Ga_2O_3, IE Cu/ZrO_2 and IE Cu/*x*-Ga_2O_3/ZrO_2]. The materials of the IW series were dried at 383 K (4 h), while the materials of the IE series were sequentially dried at 323 K (18 h) and then at 383 K (4 h). Finally, all the materials of both series were calcined (673 K, 2 h).

In another two completing series, gallia was incorporated by IW, in the same mass percentages indicated above but *after* the IE addition of copper to the zirconia, with either just further drying [series *x*-Ga_2O_3/IE Cu/ZrO_2 (D)] or drying and calcining [series *x*-Ga_2O_3/IE Cu/ZrO_2] prior to the impregnation of the gallium nitrate. Similar drying and final calcining treatments were applied to these series as well. The metal dispersion, about 3% in every case, was measured by frontal chromatography at 318 K, using 0.067 wt% N_2O/He, after H_2 prereduction at 553 K (2 K/min, 2 h) [6].

For catalytic testing, each sample (~0.1 g) was prereduced in pure hydrogen at 553 K (2 K/min, 2 h) in a microtubular plug-flow reactor. Afterwards, under hydrogen flow, the reactor was cooled to the reaction temperature (523 K) and pressurized (3 MPa). Two ternary gas mixtures were used: $H_2/CO_2/CO$ = 75/22/3 (v/v) (labeled M1) during 20 h, to evaluate possible changes in activity and/or selectivity, followed by another one where CO was substituted by helium: $H_2/CO_2/He$ = 75/22/3 (labeled M2).

Hydrogen temperature-programmed reduction (TPR) evaluation was performed in a Ohkura (TP2002-S) unit. Samples of each catalyst (0.1 g) were reduced under 5% H_2/Ar flow (30 ml/min) with a heating rate β = 8 K/min. XPS spectra of the catalysts, after in situ oxidizing (523 K under flowing 5%O_2/Ar, 10 min; β = 5 K/min), and then reducing pretreatments (553 K under flowing 5%H_2/Ar, 20 min; β = 5 K/min), were obtained with a UNI-SPECS electron spectrometer using an aluminum anode and a PHOIBOS 150 hemispherical analyzer, operating in the fixed analyzer transmission (FAT) mode (pass energy of 30 eV). Spectral processing was performed with CasaXPS software (Casa Software Ltd., UK). The samples were deliberately H_2-reduced at 553 K, as this was the temperature used to activate the catalysts prior to evaluating their performance. Binding energy (BE) values were referenced to the C1s peak (285 eV); all measurements were done at 313 K.

The impact on the metallic function upon exposing the reduced catalysts to CO was further studied by photoelectron spectroscopy (XPS) and Fourier-transformed infrared spectroscopy (FTIR) over a selected set of samples, that is, IW Cu/ZrO_2, 6-Ga_2O_3/IE Cu/ZrO_2 and IW Cu/Ga_2O_3. For XPS evaluation, after the reducing pretreatment with 5%H_2/Ar the samples were exposed to flowing 1% CO/He at 298 K (15 min) in the pre-chamber, followed by evacuation prior to acquiring spectra. Next, the samples were exposed to the stream of 1% CO/He at 673 K (5 min; β = 8 K/min) and then cooled to 313 K under flow of this gas mixture, after which new spectra were acquired.

Transmission FTIR spectra (resolution = 4 cm^{-1}) were acquired in a Nicolet Magna 550 spectrometer using a conventional, heatable and evacuable cell with NaCl windows. Thin catalysts wafers (50 mg, 1 cm dia.) were analyzed in situ after being oxidized at 673 K in flowing 10% O_2/He (5 min; β = 8 K/min) and reduced at 553 K in flowing H_2 (30 min; β = 5 K/min) afterwards, with further cooling in each case to 313 K in flowing He. After the pretreatment, a 1% CO/He stream was introduced at 313 K (15 min), with further heating to 673 K (5 min; β = 8 K/min) and then cooling back to 313 K under this gas mixture flow.

3. Results and discussion

Table 1 summarizes the pseudo steady-state performances for the methanol synthesis (i.e., reaction rate to methanol, R_{MeOH}, selectivity to methanol, S_{MeOH}, and conversion of CO_2, X_{CO_2}) of the most representative catalysts of the prepared series, obtained in the microtubular reactor at 3 MPa and 523 K using the ternary mixtures M1 ($H_2/CO_2/CO$) and M2 ($H_2/CO_2/He$) under differential conversion conditions. Fig. 1 shows the evolution with time of X_{CO_2} for these

Table 1
Activity and selectivity to methanol and carbon dioxide conversion of the Cu–Ga–Zr catalysts.[a]

Catalyst[b]	S_{BET} (m^2/g)	Reaction mixture					
		M1: $H_2/CO/CO_2$ = 75/3/22[c]			M2: $H_2/He/CO_2$ = 75/3/22[d]		
		$R_{MeOH} \times 10^8$ (mol/g_{cat} s)	S_{MeOH}[e] (%)	X_{CO_2} (%)	$R_{MeOH} \times 10^8$ (mol/g_{cat} s)	S_{MeOH}[e] (%)	X_{CO_2} (%)
IW Cu/ZrO_2	10	113	69	1.08	101	69	0.99
IW Cu/Ga_2O_3	71	80.2	69[f]	0.95	73.3	58[g]	1.09
IW Cu/6-Ga_2O_3/ZrO_2	3	115	90	0.84	114	78	0.94
6-Ga_2O_3/IE Cu/ZrO_2	8	118	73	1.07	112	72	1.05
6-Ga_2O_3/IE Cu/ZrO_2 (D)	11	79.9	72	0.73	72.2	75	0.65

[a] Operating conditions: 3 MPa, 523 K, GHSV ~ 20,000 h^{-1}.
[b] The metal dispersion on each catalyst was: D_{Cu} ~ 3% (by N_2O titration at 318 K [6]).
[c] After 20 h on stream.
[d] After 4 h on stream.
[e] S_{CH_3OH} in the column heading stands for "total selectivity to methanol".
[f] Partial values were: S_{CH_3OH} = 56.5%; S_{DME} = 13% (DME stands for dimethyl ether).
[g] Partial values were: S_{CH_3OH} = 46.5%; S_{DME} = 11%.

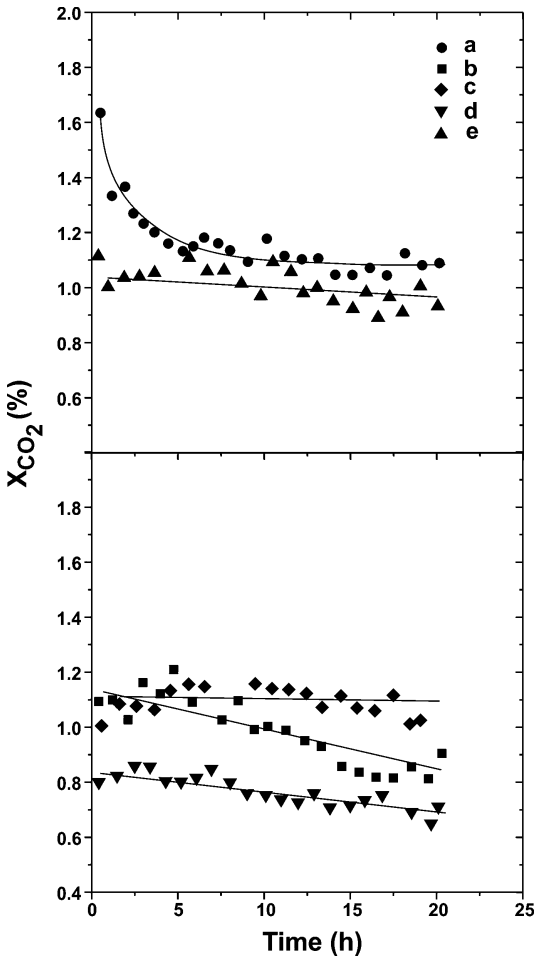

Fig. 1. Percent conversion of CO_2 (X_{CO_2}%) vs. elapsed time for the binary and ternary catalysts: (a) IW Cu/ZrO_2, (b) IW $Cu/6\text{-}Ga_2O_3/ZrO_2$, (c) $6\text{-}Ga_2O_3$/IE Cu/ZrO_2, (d) $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D), and (e) IW Cu/Ga_2O_3. Operating conditions: P = 3 MPa; T = 523 K; GHSV = 20000 h^{-1}, M1 mixture ($H_2/CO_2/CO$ = 75/22/3).

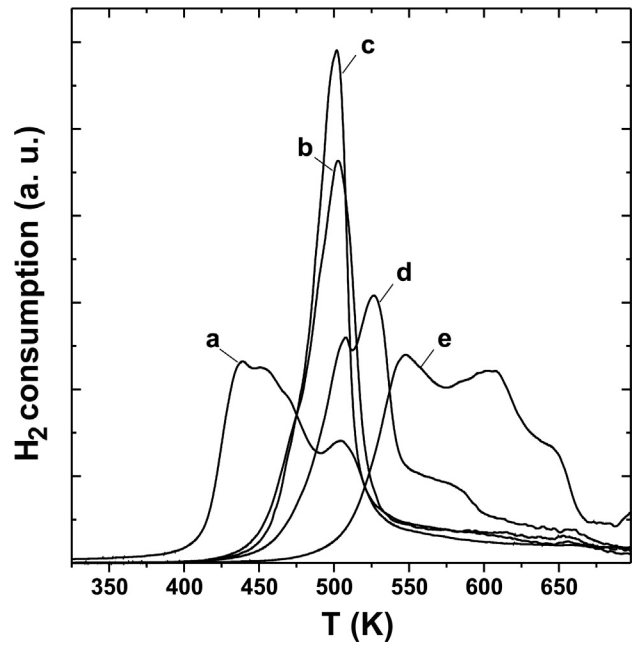

Fig. 2. TPR profiles of the calcined catalysts: (a) IW Cu/ZrO_2, (b) IW $Cu/6\text{-}Ga_2O_3/ZrO_2$, (c) $6\text{-}Ga_2O_3$/IE Cu/ZrO_2, (d) $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D), and (e) IW Cu/Ga_2O_3.

binary and ternary catalysts upon using the reaction mixture M1. Only the ternary catalysts containing 6 wt% gallia are considered here because the performance variation within the different series was minimal, whereas significant – and relevant-distinctive trends were observed amongst them. The performance of the complete set of prepared catalysts can be found elsewhere [2].

The binary catalyst IW Cu/ZrO_2 showed much better activity to methanol than the IW Cu/Ga_2O_3 did, but the activity of the former was not stable with time. As regards the ternary materials, the catalyst wherein the copper was added onto the Ga_2O_3/ZrO_2 support (IW $Cu/6\text{-}Ga_2O_3/ZrO_2$), as well as the catalyst in which gallium nitrate was impregnated onto the dried *and* calcined IE Cu/ZrO_2 ($6\text{-}Ga_2O_3$/IE Cu/ZrO_2) showed higher R_{MeOH} and S_{MeOH}, being the last one the most stable of both. However, the material where gallium nitrate was added by IW onto the dried Cu/ZrO_2 after the ion exchange of copper [$6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D)] showed a poorer rate to methanol, albeit still showing a better stability than IW Cu/ZrO_2.

The better performance of the IW $Cu/6\text{-}Ga_2O_3/ZrO_2$ and $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 ternary catalysts suggests, quite strongly, on the convenience of putting together the metal with both 'supports'. The better stability of the ternary catalysts in comparison with the binary IW Cu/ZrO_2 preparation agrees fairly well with the observations of Toyir et al. [7], who reported a higher stability of $Cu–Zn–Ga/SiO_2$ catalysts than their $Cu–Zn/SiO_2$ counterparts, without gallia.

Therefore, to gain a deeper knowledge on the underlying causes of the different catalytic behavior observed in the methanol synthesis from these materials, hydrogen TPR was first performed. Fig. 2 shows the TPR profiles of the IW Cu/ZrO_2, IW Cu/Ga_2O_3, IW $Cu/6\text{-}Ga_2O_3/ZrO_2$, $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 and $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D) catalysts, in which distinct reduction peaks are observed in the 437–693 K temperature range. The catalyst IW Cu/ZrO_2 presented the lowest reduction temperatures of the set (especially in relation to IW Cu/Ga_2O_3). This reduction pattern indicates the existence of a high initial dispersion of the copper particles on the circonia, together with a just moderate interaction $CuO–ZrO_2$, which facilitates the reduction of the metal on this oxide. This is in accordance with similar observations of Natesakhawat et al. and Zhang et al. [8,9], especially considering that bulk CuO is usually hydrogen-reduced between 573 and 593 K [8,10].

On the other hand, the ternary catalysts IW $Cu/6\text{-}Ga_2O_3/ZrO_2$ and $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 showed similar behavior and intermediate reduction temperatures than those of the binary ones. This suggests that it might be irrelevant whether the copper is incorporated to the (calcined) mixed oxide (Ga_2O_3/ZrO_2) or the gallia is added onto the dried and calcined Cu/ZrO_2 after the ion exchange of the metal complex. At variance, the $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D) material showed higher reduction temperatures, closer to those of IW Cu/Ga_2O_3, what in 'classic' terms suggests the presence of larger CuO particles or – more likely – a strong interaction between the copper and the gallia possibly due to the formation of a $CuGa_2O_4$ spinel. Indeed, Faungnawakij et al. [11] reported a TPR profile similar to the one obtained in this work with the IW Cu/Ga_2O_3 catalyst in their study by XRD, XPS and TPR of the $CuGa_2O_4$ spinel. Secondly, the reduction temperatures of the $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D), closer to the TPR pattern of the binary IW Cu/Ga_2O_3 catalyst, also indicate the preferential deposition of the gallia near the copper oxide domains in this case. That is, when just a drying treatment – rather than drying and calcining – was applied to the Cu–Zr precursor. The reduction peaks observed above 625 K in the IW Cu/Ga_2O_3 and $6\text{-}Ga_2O_3$/IE Cu/ZrO_2 (D) catalysts could well be associated to the reduction of a segregated Ga_2O_3 phase, since bulk gallium oxide presents a wide

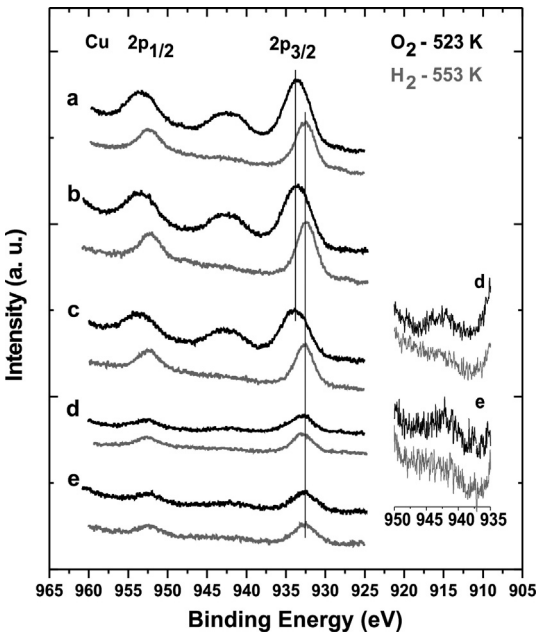

Fig. 3. Cu 2p XPS spectra of the binary and ternary catalysts, calcined at 523 K (10 min) under flowing 5%O_2/Ar (black traces) and reduced at 553 K (20 min) under flowing 5% H_2/Ar (gray traces): (a) IW Cu/ZrO_2, (b) IW Cu/6-Ga_2O_3/ZrO_2, (c) 6-Ga_2O_3/IE Cu/ZrO_2, (d) 6-Ga_2O_3/IE Cu/ZrO_2 (D), and (e) IW Cu/Ga_2O_3.

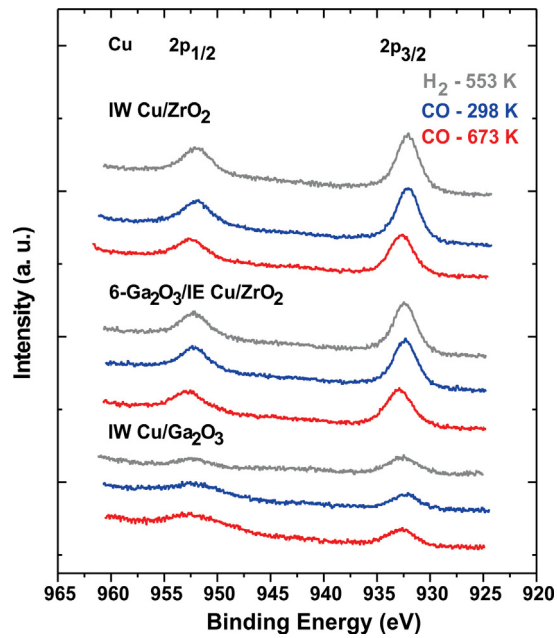

Fig. 4. Cu 2p XPS spectra of the indicated, selected set of catalysts after the adsorption of 1%CO/He at 298 K (15 min) and 673 K (5 min), followed by cooling down onstream to 313 K on each case. Catalysts pretreatment: 5%O_2/Ar at 523 K (10 min), followed by 5%H_2/Ar at 553 K (20 min).

reduction peak that starts at 600 K, the maximum reduction being reached around 870 K [12].

Finally, the reduction temperatures observed for the IW Cu/Ga_2O_3 and 6-Ga_2O_3/IE Cu/ZrO_2 (D) catalysts, between 580 and 610 K, indicate that it would take temperatures above 553 K to fully activate the metallic function under flowing hydrogen in these materials, unlike the rest of the catalysts evaluated. This fact could explain, in part, the lower catalytic performance in the methanol synthesis observed on these catalysts.

Fig. 3 shows the Cu 2p XPS spectra of the oxidized and reduced catalysts. The spectra of the IW Cu/ZrO_2, IW Cu/6-Ga_2O_3/ZrO_2 and 6-Ga_2O_3/IE Cu/ZrO_2 oxidized materials show the binding energy (BE) values at about 933.5 eV and the satellite peaks at 942.7–941.5 eV characteristic of the $2p_{3/2}$ spectrum of Cu^{2+} [13]. The lower BE of the Cu $2p_{3/2}$ signals, in relation to the values exhibited by pure CuO (934.0 eV [14]), suggests that in every case certain degree of interaction between the CuO domains and the supports was achieved [15]. The satellite peaks disappeared in those reduced samples simultaneously with the shift of Cu $2p_{3/2}$ peak to ~932.6 eV, thus implying that after the H_2 reduction at 553 K the Cu^{2+} ion was reduced to Cu^+/Cu^0, since the reference BE values for Cu_2O and Cu are practically indistinguishable (932.6 and 932.8 eV, respectively [16]).

At variance with the catalysts mentioned in the former paragraph, no significant BE shift was observed in the Cu 2p peaks of the oxidized vs. the reduced samples of the catalysts where the highest intimacy copper–gallia was expected, namely: IW Cu/Ga_2O_3 and 6-Ga_2O_3/IE Cu/ZrO_2 (D), which strongly suggests the surface formation of a $CuGa_2O_4$ spinel on these. The Cu $2p_{3/2}$ BE value was approximately 932.8 eV for either of these catalysts, with the typical satellite peak of Cu^{2+} (942.7–941.5 eV) only present in the oxidized materials, which disappeared after reduction suggesting the formation of Cu^+/Cu^0. In addition, the lower intensity of the Cu 2p peaks for these materials is consistent with the hypothesis of formation of a $CuGa_2O_4$ spinel during the synthesis which, in line with similar findings recently published [11], would cause a decrease in the amount of superficial copper available to supply the metallic function in the methanol synthesis and/or would impair the mobility of chemisorbed surface intermediates. Altogether, this means that an 'excessive interaction' between copper and gallia might not be appropriate for an efficient synthesis of the alcohol. Unfortunately, the Ga 2p XPS spectra of the oxidized vs. the reduced catalysts were of no help to discern any impact of the gallia-copper interaction (see supplementary information).

To exclude the possibility of an inadvertent and undesired reduction of the copper during the cooling under vacuum of the calcined samples, an additional measurement was performed on the IW Cu/Ga_2O_3 catalyst, but cooling down to 343 K under flowing 5% O_2/Ar prior to evacuating. Again, as in the previous experiment, no meaningful shift of the BE of the Cu 2p peak was observed, thus allowing to discard the likelihood of copper reduction due to experimental artifacts.

Further information on the effect of a reducing atmosphere on the metallic function (copper crystallites sintering, in particular) over a selected set of oxidized and H_2-prereduced catalysts at increasing temperature was obtained by XPS using 1%CO/He (Fig. 4), since it is well documented that CO – a reactant present in the methanol synthesis reaction – is able to reconstruct and even cause sintering of the copper particles [17]. First, Table 2 neatly shows that the decrease of the surface fraction of copper upon H_2-reduction at 553 K, as determined by this surface technique, was pronounced on the binary circonia-supported catalyst, that is 4.8 (reduced) versus 7.7 (oxidized), which means a ~60% decrease of XPS detected copper. However, the lower impact of the H_2 reduction observed in the gallia-supported preparations (~30% of Cu surface fraction decline) might be due to the stronger interaction of the copper with these Ga_2O_3-containing supports. More interestingly, the H_2-reduced IW Cu/ZrO_2 catalyst suffered a detectable diminution in copper surface fraction after CO exposure at 673 K, much higher than the one on the ternary 6-Ga_2O_3/IE Cu/ZrO_2 catalyst (the change on the binary IW Cu/Ga_2O_3 catalyst was undetectable), which might be, once more, indicative of the strong Cu–Ga_2O_3 (nano spinel?) interaction that gave the gallia-promoted ternary catalysts the highest stability of the set while preserving a reasonable activity of them.

Table 2
Atomic superficial fraction of copper after oxidation and/or reduction treatments and after exposure to CO (XPS values), and estimated surface fraction of Cu^+ and Cu^0 (IR values).

Catalyst	Cu/(Cu + Ga + Zr)[a] (%)				$Cu^+/(Cu^+ + Cu^0)$[b] (%)	Total integrated absorbance [ν(CO)][c]
	O_2-523 K	H_2-553 K	CO-298 K	CO-673 K	CO-313 K	Initial/final
IW Cu/ZrO_2	7.7	4.8	4.7	3.7	8	16.4/4.8
6-Ga_2O_3/IE Cu/ZrO_2	5.2	3.3	3.5	3.0	17	14.8/4.9
IW Cu/Ga_2O_3	1.5	1.1	1.1	1.1	52	14.2/19.7

[a] XPS signals: Cu ($2p_{3/2}$), Ga ($2p_{3/2}$) and Zr ($3d_{5/2}$). O_2: oxidation at 523 K; H_2: reduction at 553 K, CO: adsorption of 1%CO/He after each of the indicated pretreatments, at the given temperatures: 298 or 673 K. XPS measurements were done after cooling down to 313 K under the CO/He gas mixture.
[b] IR signals: Cu^+ (2125 cm^{-1}) and Cu^0 (2100 and 2070 cm^{-1}, corresponding to low and high coordination sites, respectively). Values measured on reduced samples (H_2, 553 K) after CO adsorption (1%CO/He) at 313 K.
[c] Values obtained from IR spectra recorded at 313 K before heating [initial] and after cooling [final] (up to 673 and 313 K, respectively) under 1%CO/He gas mixture.

Regrettably, it was not possible to carry out a reliable discrimination of the copper oxidation state(s) over the reduced catalysts (viz., Cu^+ and/or Cu^0) by means of XPS, using the Cu-LMM Auger spectral region, due to the superposition of these signals with those of the pure supports: ZrO_2 (oxygen plasmon loss, at 914.9 eV [14,18]), and Ga_2O_3 ($L_3M_{23}M_{23}$, at 919.6 eV [16]). However, we were able to identify the presence of both copper species on the catalysts' surface by means of CO chemisorption as a molecular probe, using FTIR. Also, the effect of a reducing atmosphere such as the CO on the metallic function 'copperí (especially sintering) over the reduced catalysts was further confirmed by IR, as described below.

The interaction of CO with the surface of the H_2-reduced selected catalysts developed relatively broad infrared bands in the 2150–2070 cm^{-1} region (Fig. 5). For the lower wavenumbers, the signals were ascribed to the stretching C—O mode of linearly chemisorbed CO on metallic copper (Cu^0) with different coordination numbers, that is, small Cu crystallites or rough Cu crystal plane [e.g., (2 1 1), (3 1 1) and (7 5 5)] at ~2100 cm^{-1} and densely packed planes [e.g., (1 1 1), (1 0 0) and (1 1 0)] at ~2060 cm^{-1}. In addition, the band at ~2125 cm^{-1} was attributed to the linear vibration of CO on Cu^+ sites ([19–21], and references therein). Although at 313 K the total integrated absorbance of the CO convoluted bands [ν(CO)] was similar for the selected set of reduced catalysts (initial values, last column in Table 2), the Cu^+ sites prevail on the IW Cu/Ga_2O_3 catalyst and are noticeably more abundant on the ternary catalyst than on IW Cu/ZrO_2 (see Cu^+ fractional composition in Table 2 and deconvoluted bands in Fig. 5), which is proper of the high copper–gallia nano-interaction, as suggested before.

Concurrently, the thermal evolution of the ν(CO) signals followed different and distinctive patterns for each catalyst. After heating the pre-reduced catalysts up to 673 K and then cooling back to 313 K, under 1%CO/He flow, the total integrated absorbance of ν(CO) decreased about 70% for IW Cu/ZrO_2 and Ga_2O_3/IE Cu/ZrO_2 (see Table 2), that is, the catalysts in which copper–zirconia intimacy was controlling. Conversely, the strong copper–gallia interaction in IW Cu/Ga_2O_3 prevented any ícopperí sintering, as no decay of the integrated absorbance occurred there while, on the contrary, higher absorbance was observed (maybe due to some copper segregation from the spinel structure, see final values, last column in Table 2).

Furthermore, even though the decrease in IR signals upon heating owing to CO desorption maybe convoluted with metal sintering, the zirconia-supported binary catalyst was the most strongly affected material by the presence of CO in the 500 K temperature region (Fig. 6), above which temperature no adsorbed CO was detected. On the contrary, higher intensity of CO IR signals for the gallia-containing catalysts, at the methanol synthesis temperature (523 K), revealed a better retention of the ícopperí dispersion, then and again, supporting the hypothesis of copper gallate nano-spinel formation as a prerequisite to avoid copper sintering and to sustain the catalystsí activity under reaction conditions.

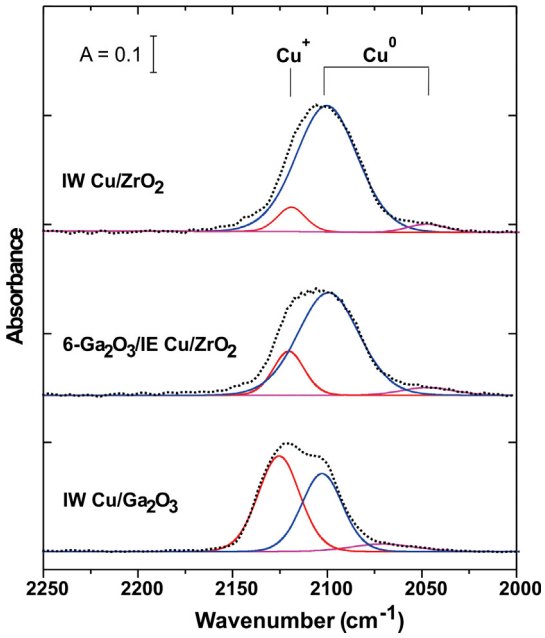

Fig. 5. Infrared spectra of adsorbed CO on copper sites over the indicated, selected set of catalysts, measured at 313 K. Catalysts pretreatment: 10%O_2/He at 673 K followed by H_2 at 553 K.

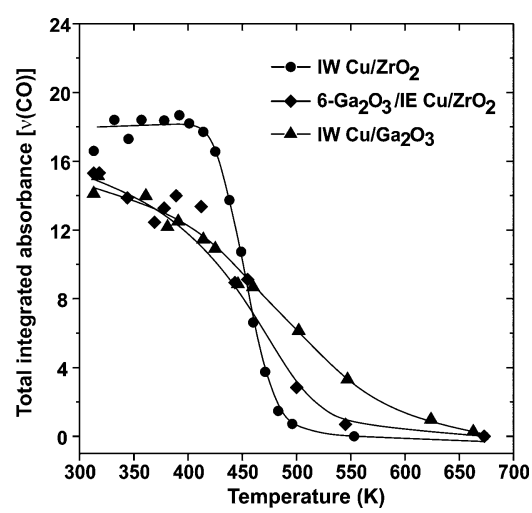

Fig. 6. Thermal evolution of the total integrated absorbance of the ν(CO) bands on copper versus the adsorption temperature (heating ramp: 8 K/min) under 1%CO/He flow over the selected set of. catalysts: catalysts pretreatment: 10%O_2/He at 673 K followed by H_2 at 553 K.

4. Conclusions

It is postulated that maximizing the Cu–Ga_2O_3 interaction (with the likely formation of a $CuGa_2O_4$ nanospinel) in the prepared ternary Cu–Ga_2O_3–ZrO_2 catalysts prevents both the sintering of the metal particles and the complete reduction of copper, whereas prioritizing the Cu–ZrO_2 interaction leads to improved reducibility of the copper particles.

The reduction of the catalysts with hydrogen before their exposition to CO avoids the sintering of the copper particles at low temperature, especially whenever the interaction Cu–Ga_2O_3 is negligible. However, under typical methanol synthesis conditions said Cu–Ga_2O_3 interaction becomes beneficial in terms of catalytic performance, because the 'metal' dispersion is better preserved then.

Clearly, a balance of both interactions, Cu–ZrO_2 and Cu–Ga_2O_3, in the ternary Cu–Ga_2O_3–ZrO_2 catalysts allows to maximize the amount of superficial metallic copper available to carry out the selective hydrogenation of carbon oxides to methanol with a best, stable performance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.11.021.

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